THE RHEOLOGICAL BEHAVIOR ANALYSIS OF GREEN SYRUPS PRODUCED AT RAW CANE SUGAR REFINING

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ABSTRACT

The viscosity of food fluids is one of the most important parameters required in the design of technological processes in food industries. The rheology of thick juice and two green syrups was studied using AR 2000ex rheometer. The syrups were studied at 4°C, 8°C and 12°C and the viscosity, the rate index and the hysteresis area were determined under forced flow conditions. Obtained data were fitted by the power law model. Viscosity and shear stress values varied with temperature, decreasing with the rise of thesyrups temperature. The thixotropy was recorded for all the analyzed samples, but with small hysteresis aria values. The flow process and the recovery of studied syrups structure had maximum values at temperature of 4 ºC. The thick juice behaved as a non-Newtonian fluid and the green syrups behaved as a complex fluid with a viscous component that induced a predominant Newtonian flow at high shear rates. The apparent viscosity decreased with increasing temperature and shear rate, implying that the studied syrups behaved as shear thinning materials.

Key words: Green syrup; Thick juice; Power law; Newtonian fluid; Viscosity.

INTRODUCTION

Syrups from sugar industry (thick juice, run-off syrup/green syrup) and molasses are used for other industrial purposes, mainly as fermentation processes (citric, lactic, oxalic or glutamic acid, lysine), particle binding, bio-ethanol or gasohol production (Solomon, 2011; Krajnc and Glavič, 2009). After sterilization they have to cool down at low temperatures for their storage. The optimum storage temperature varies from 0 °C to 10 °C (Sargent *et al*., 1997).

For sugar production, the sugar cane industry can use a three-stage crystallization. The purpose of the crystallization technology is to recover the maximum amount of sucrose from thick juice and produce low-purity molasses. The syrups involved in the three-boiling scheme or in so-called tree-stage crystallization are the thick juice, the high-green syrup, and the low-green syrup. The syrups are characterized by a viscosity that influences the liquid flow, the pumping, heating, cooling, etc. Before first stage of crystallization, the standard liquor is boiled until supersaturating, which means that at temperatures of around 20 ºC the syrup is unsaturated. After the first stage of crystallization and centrifugation the high-green syrup or the A-green syrup is obtained and after the second stage of crystallization and centrifugation the low-green syrup or the B-green syrup is produced. Those syrups are also unsaturated sucrose solutions, which beside sucrose, have small amounts of other saccharides (glucose, fructose, kestose, raffinose), polysaccharides (starch, gums, dextrans, levans), non-sugar components such as proteins, amino acids, nitrates, nitrites, pigments (flavonoids, polyphenols), minerals and trace elements, vitamins (van der Poel *et al*., 1998).

Viscosity is a physical property of sugar syrup that can influence the operation and performance of a sugar refinery. Barker (1998) studied different pure sucrose solutions and final molasses. In the case of pure sucrose solutions (60 to 65 °Bx), the cone and plate viscometer confirms the Newtonian behavior of the solutions ($n = l$), whereas the disc spindle viscometer reads the solution as non-Newtonian ($n = 1.4$). Also, it was found that the cone and plate viscometer showed that the final molasses are closer to Newtonian behavior ($n = 0.9$) when compared with the disc spindle viscometer (values of 0.6 to 0.8). Another important conclusion is that when increasing the temperature of molasses the consistency decreases exponentially and thus the more viscous the molasses, the greater the effect. Zailer (2011) found that sugarcane juice exhibits a Newtonian behavior in flow for a range of temperatures between 277 and 373 K (4 to 100 °C). He found that the viscosity values lower as the temperature increases.

There are fluids that have a non-Newtonian behavior such as aqueous solution of sucrose, glucose and fructose (Telis *et al*., 2007) supersaturated sucrose solutions (Quintas *et al*, 2006). The knowledge of the flow behavior of a fluid is useful in engineering applications that are related to the equipment design and unit operations, as well as for the understanding of the transport processes (Chhabra and Richardson, 2011).

Our study was done due to the lack of published information concerning the rheological behaviour of the syrups (thick juice, A-green syrup, B-green syrup) at low temperatures. The thick juice, the A-green syrup and the

B-green syrup can be used industrially for other purposes besides sugar production, such as for bio-ethanol production, biomass production or as nutritive supplement for animal feed. Also, in the case of technological problems or process interruptions, the syrups can be cooled at low temperatures to avoid microbial fermentation and further processed. So, we are interested in finding those syrups rheological properties at low temperatures.

MATERIALS AND METHODS

Syrups characterization: Sugarcane thick juice, A-green syrup and B-green syrup were provided by a Romanian sugar factory. They were taken from crystallization stages, the factory working with the three-stage crystallization or three-boiling technology. The thick juice is purified to a product called massecuite A. The massecuite A is centrifuged to obtain sugar product A and green syrup A. The green syrup A is then dissolved and purified to obtain the massecuite B. The massecuite B is centrifuged resulting the sugar product B and green syrup B.

For each syrup the dry weight was determined as the soluble solids (S.S.), expressed as °Bx, with a digital refractometer HI 96800 (Hanna Instruments, Italy), the sugar amount as polarizable sugars, expressed as Pol., with P-2000 polarimeter (Jasco, Japan) and the apparent purity was calculated as (Pol. / °Bx) x 100. The syrups were analyzed according to the standards used in the sugar industry (STAS 12871-90, 1990). The values were obtained in triplicate and the main values are presented in table 1.

Table 1. The apparent values for the sucrose, the dry weight and the purity of analyzed syrups

Syrup	Pol.	S.S. (°Bx)	Purity (%)
Thick juice	89.26	91.5	97.56
A-green syrup	77.24	82	94.2
B-green syrup	72.32	82	88.2

Rheological analysis: Before rheological measurements, the syrups were homogenized by stirring. The analyses were carried out using an AR 2000ex rheometer (TA Instruments, New Castle, DE) with CP2/40 (cone-plate with 40 mm diameter and 2° angle) measuring system and a gap of 1 mm. The AR 2000ex rheometer is equipped with a Peltier plate for the temperature control within the gap. The syrups were cooled at 4 °C, 8 °C and 12 °C. Applying the stepped flow test the variation curves for shear stress, viscosity and shear rate were obtained. The instrument was set to apply shear rates ranging from 0.1 to 100 s^{-1} and the upward and downward test was performed in triplicate for each syrup and temperature. The flow model used to characterize the flow process was the power law model. It gives us an insight into the shear-thinning and shear thickening fluids. With the help of Rheology Advantage Data Analysis Software v. 5.5.2.0 were set the work parameters for the AR 2000ex rheometer. The data were analyzed obtaining the apparent viscosity, the hysteresis area and the flow index values. With the Excel software from Microsoft Office 2010 pack, the graphical results for shear stress, shear rate and viscosity were made.

Statistical analysis: The statistical interpretation of the results was performed using ANOVA Single Factor ($\alpha = 0.05$) in Excel (Microsoft Office 2010). Statistical analysis for differences between groups was performed by using the Fisher Least Significant Difference (LSD) test.

RESULTS AND DISCUSSION

The viscosity, the rate index and the hysteresis area were determined for the three sugarcane syrups. The viscosity of a fluid provide us with information about the internal frictions that influence the production and transportation processes. Also, the viscosity is a function of the intermolecular forces that restrict molecular motion. These forces depend on the intermolecular spacing which determines the free volume and are affected by change in temperature (Toğrul and Arslan, 2004). The rate index (flow behavior index) gives an idea about the type of fluid that can behave as Newtonian or non-Newtonian (Earle, 2013). The presence of a hysteresis in the flow curve tells us that the shearing at high shear rate modifies the structure of the fluid (Norton *et al*., 2010). It is determined basedon the shear stress-shear rate variation. The presence of the hysteresis loop is an indication of the shearing effect on the molecular structure of the syrups (Habibi-Najafi and Alaei, 2006). The viscoelastic parameters of the analyzed syrups at 4 °C, 8 °C and 12 °C were determined for the upward and downward curves and presented in the tables 2, 3 and 4. For each cooled syrup analyzed the graphical variations of viscosity-shear rate and the shear stress-shear rate in figure 1, 2 and 3 were determined.

From the data presented in table 2 one can see that the viscosity of the thick juice was higher, possibly due to the high amount of sucrose (sugar) and the presence of non-sugar components. The amount of sucrose seems to especially influence the viscosity of the syrups because the thick juice has a higher amount of sucrose compared with the green syrups. As Nindo *et al.* (2005) determined, the amount of dissolved solids has a stronger influence on the viscosity of the juices. The temperature value influenced the viscosity of the juices, as presented in tables 2, 3 and 4, the increase of the temperature making the juices less viscous.

The flow behavior index (n) for the sugarcane syrups also presented variations. It is known that for the power law model when $n = 1$ a fluid is Newtonian, when $n > 1$ the fluid show shear-thickening behavior and when $n < 1$ the fluid exhibit shear-thinning behavior. When $n \neq 1$ the fluid is a non-Newtonian fluid (Chhabra and Richardson, 2011). At 4 °C and 8 °C the A and B-green syrups presented a non-Newtonian behavior for the up curve and a Newtonian behavior for the down curve. At 12 °C only the B-green syrup presented such a behavior. For all the temperatures the thick juice presented a non-Newtonian behavior, acting as a pseudoplastic fluid.

Considering the rheograms from figure 1 and the values presented in table 2, 3 and 4, it can be seen that the viscosity ofthe cooled thick juice decreased with the temperature increase. We appreciate that this is due to the interaction between the particles which decreases the viscosity at lower solids concentration (Toğrul and Arslan, 2004). Also, at higher temperatures the thermal energy of the molecule increases with the increase of intermolecular distances, causing reduction of intermolecular forces and consequently, the viscosity decreases (Holdsworth, 1971). Comparing the viscosity values of the thick juice with the values of the other analyzed juices, the thick juice presented the highest viscosity values. Rate index (n) values are less than one which indicates a fluid with non-Newtonian behavior. As indicated in the tables the index is $n < 1$, so, the cooled thick juice presented a shear-thinning behavior. This behavior is due to the high amount of sugar and non-sugar components of the juice. As seen in figure 1 for shear stress and shear rate variations, the cooled thick juice need a higher stress at 4°C in order to initiate flow. From table 2, 3 and 4, it can be seen that of all samples the thick juice exhibited the highest hysteresis area. According to Razavi *et al.* (2010) the presence of hysteresis area means that shear stress-shear rate relationship is non-linear due to the structure breakdown.

Table 2. Viscoelastic parameters of the syrups at 4 ˚C.

Sample type	Up curve			Down curve		
	Viscosity (Pa·s)	Rate index	Hysteresis (Pa/s)	Viscosity (Pa·s)	Rate index	Hysteresis (Pa/s)
Thick juice	0.284±0.02^{a}	0.984±0.00^{a}	10.181±2.91^{a}	0.268±0.01^{a}	0.996±0.00^{a}	10.181±2.91^{a}
A-green syrup	0.253±0.00^{ab}	0.989±0.00^{a}	8.540±3.15	0.238±0.00^{ab}	1.001±0.00^{a}	8.540±3.15
B-green syrup	0.079±0.00^{ab}	0.992±0.00	3.424±1.59^{a}	0.0748±0.00^{ab}	1.003±0.00^{a}	3.424±1.59^{a}
p-value	0.000	0.111	0.047	0.000	0.0001	0.047

Values represent means of three replicates ± Standard Deviation

Means with same superscript within same column differ significantly ($p<0.05$)

Table 3. Viscoelastic parameters of the samples at 8 ˚C.

Sample type	Up curve			Down curve		
	Viscosity (Pa·s)	Rate index	Hysteresis (Pa/s)	Viscosity (Pa·s)	Rate index	Hysteresis (Pa/s)
Thick juice	0.211±0.01^{a}	0.974±0.00^{a}	10.181±2.91^{a}	0.191±0.01^{a}	0.995±0.00^{a}	10.181±2.91^{a}
A-green syrup	0.189±0.00^{ab}	0.974±0.00^{ab}	8.540±3.15	0.164±0.00^{ab}	1.005±0.00^{a}	8.540±3.15
B-green syrup	0.061±0.00^{ab}	0.984±0.00^{ab}	3.424±1.59^{a}	0.055±0.00^{ab}	1.006±0.00^{a}	3.424±1.59^{a}
p-value	0.000	0.005	0.047	0.000	0.021	0.047

Values represent means of three replicates ± Standard Deviation

Means with same superscript within same column differ significantly ($p<0.05$)

Table 4. Viscoelastic parameters of the samples at 12 ˚C.

Sample type	Up curve			Down curve		
	Viscosity (Pa·s)	Rate index	Hysteresis (Pa/s)	Viscosity (Pa·s)	Rate index*	Hysteresis (Pa/s)
Thick juice	0.149±0.01^{a}	0.978±0.00^{a}	10.181±2.91^{a}	0.143±0.01^{a}	0.987±0.01	10.181±2.91^{a}
A-green syrup	0.130±0.00^{ab}	0.982±0.00	8.540±3.15	0.121±0.00^{ab}	0.999±0.00	8.540±3.15
B-green syrup	0.044±0.00^{ab}	0.991±0.00^{a}	3.424±1.59^{a}	0.043±0.00^{ab}	1.001±0.00	3.424±1.59^{a}
p-value	0.000	0.051	0.047	0.000	0.119	0.047

Values represent means of three replicates ± Standard Deviation

Means with same superscript within same column differ significantly ($p<0.05$)

*Means within same column did not present any statistical differences.

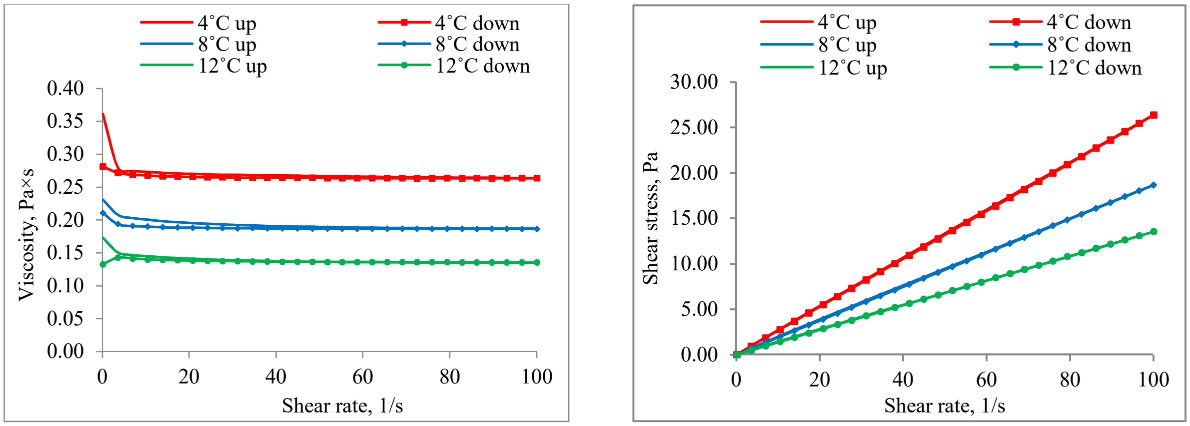

Fig. 1. The rheograms for cooled thick juice

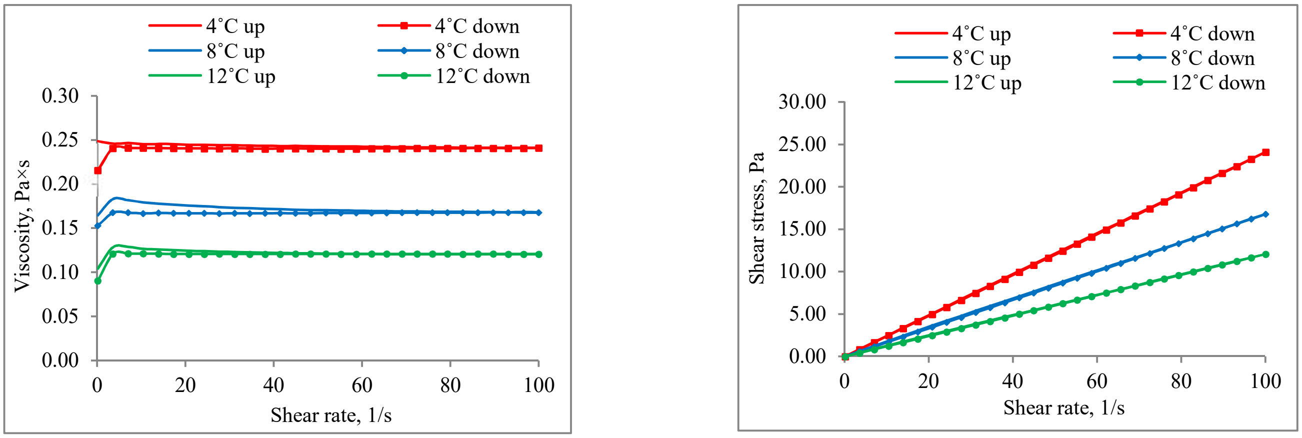

Fig. 2. The rheograms for cooled A-green syrup

From the data presented in tables 2, 3 and 4 and the rheograms from figure 2 it can be seen that the cooled A-green syrup presented the highest viscosity and a shear stress at 4 °C. Due to the values of the rate index (n) for low shear rate values the A-green syrup behaved as a non-Newtonian fluid, whereas for forced flow at shear rate values above 50 s^{-1} it behaved as a Newtonian fluid. In the food industry it is better to use Newtonian fluids because such fluids don't get stuck in the pipes, there is no need for special design of fittings for the fluid to move and the pumps won't overload. Compared with the values of cooled thick juice, the viscosity and hysteresis area are smaller. Those values were obtained because in the first crystallization phase, a certain quantity of sugar from thick juice is removed, thus resulting the A-green syrup.

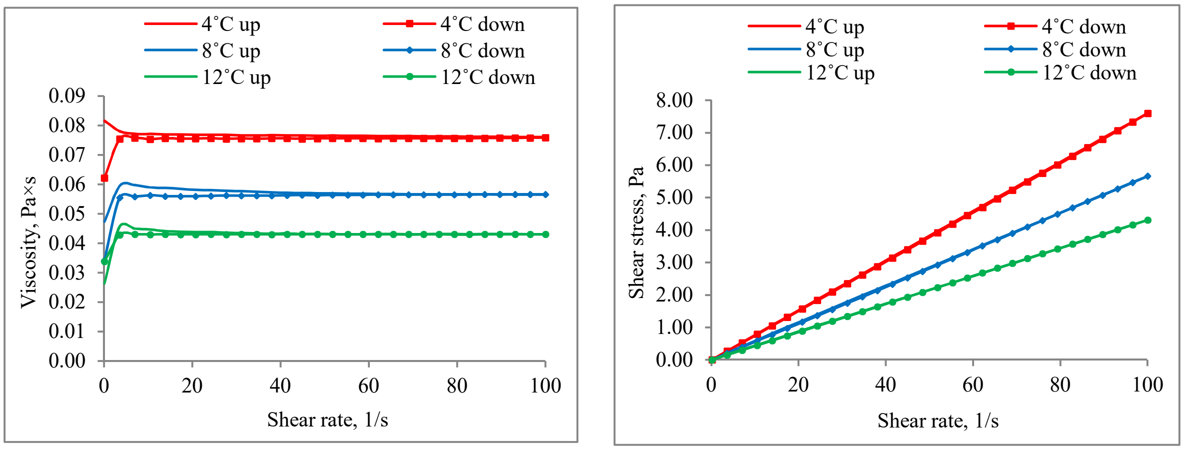

Fig.3. The rheograms for cooled B-green syrup

The dates from tables 2, 3 and 4 and the rheograms from figure 3 show that the B-green syrup has a higher viscosity and shear stress at 4 °C. The B-green syrup presented lower values of viscosity, shear stress and hysteresis when compared with the values of the A-green syrup and the thick juice. Those behaviors are due to the smaller sucrose amount and highest non-sugar amount of the B-green syrup produced in the second stage of crystallization. The values of n index showed a non-Newtonian behavior of the B syrup for reduced shear rates, but for forced flow conditions the obtained data indicated a Newtonian behavior.

Conclusions: The thick juice, the A-green syrup and the B-green syrup viscosity decreased with the temperature increase. The A-green syrup and the B-green syrup are complex fluids with a viscous component that induces a predominant Newtonian flow at high shear rates. The syrups presented a shear-thinning behavior at low temperatures that is a very important characteristic of a fluid that is transported through pipes. The flow process and the recovery of studied syrups structure had maximum values at temperature of 4 ºC. At 8 °C the viscosity of thick juice and A-green syrup increased but not exceeded the one at 4 °C. The results obtained in this study on the rheological behavior of syrups can help optimize the technological processes in bio-ethanol production, biomass production and various chemical substances production (citric acid, lactic acid etc.).

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